
CLAIMS

(57) [Claim(s)]

[Claim 1] The manufacture approach of the substrate in which precision thin-line circuit formation with the subtractive process characterized by carrying out surface metallic-coating processing by which approach of sputtering, ion plating, or vacuum deposition, heating the substrate which it comes to fabricate using the liquid-crystalline-polyester-resin constituent which makes the melting workability polyester (liquid crystallinity polyester) which can form an anisotropy melting phase come to contain an inorganic filler so that the skin temperature of a substrate may become 60 degrees C or more within a vacuum tub is possible.

[Claim 2] The manufacture approach of a substrate according to claim 1 that it is one sort or two sorts or more of fines-like inorganic fillers chosen from the group which an inorganic filler becomes from the element of a periodic table II group element and its oxide, a sulfate, phosphate, silicate, a carbonate or aluminum, silicon, tin, lead, antimony, and a bismuth, and its oxide, and the loadings are 5 – 80 % of the weight to all constituent weight.

[Claim 3] The manufacture approach of the substrate according to claim 2 which has a fines-like inorganic filler in the range of 0.01–100-micrometer mean particle diameter.

[Claim 4] The manufacture approach of a substrate according to claim 1 that an inorganic filler is a fibrous inorganic substance in the range of the diameter of 1–30 micrometers, and 5 micrometers – 1mm die length, and the loadings are 1 – 60 % of the weight to all constituent weight.

[Claim 5] The manufacture approach of a substrate according to claim 1 that one sort or two sorts or more of the fines-like inorganic fillers and fibrous inorganic substances which were chosen from the group which an inorganic filler becomes from the element of a periodic table II group element and its oxide, a sulfate, phosphate, silicate, a carbonate or aluminum, silicon, tin, lead, antimony, and a bismuth and its oxide are used together, and these total loadings are 85 or less % of the weight to all constituent weight.

[Claim 6] The manufacture approach of a substrate according to claim 4 or 5 that a fibrous inorganic substance is a glass fiber, a milled glass fiber, or a potassium titanate fiber.

[Claim 7] The manufacture approach of the substrate according to claim 1 fabricated by fabrication means by which a substrate is chosen from among injection

molding, extrusion molding, and compression molding.

[Claim 8] The manufacture approach of a substrate according to claim 1 that a substrate is an object for pin grid arrays (PGA), or a substrate for shaping printed circuits.

[Claim 9] The manufacture approach of a substrate according to claim 1 that a substrate has the shape of a solid configuration, the shape of a film, and a sheet.

[Claim 10] The substrate in which precision thin line circuit formation with the subtractive process acquired by which manufacture approach of claims 1-9 is possible.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application]

the melting workability polyester with which this invention can form an anisotropy melting phase -- " -- it only abbreviates to "liquid crystallinity polyester" henceforth -- it is related with the substrate obtained by the surface metallic-coating approach and approach of the substrate which can form the precision thin line circuit by the subtractive process which it comes to fabricate using a resin constituent.

Furthermore, it is related with the substrate created by the substrate fabricated in detail using the liquid-crystalline-polyester-resin constituent which was excellent in thermal resistance and fabrication nature as a substrate for precision thin line circuit formation by the subtractive process by the approach of carrying out surface metallic-coating processing efficiently, and its approach.

[Description of the Prior Art]

Unlike the thermoplastic polyester generally known, for example, polybutylene terephthalate, and polyethylene terephthalate, liquid crystallinity polyester consists of an upright macromolecule, and also in the state of melting, since the shape of a rod is maintained that it is hard to bend, as for a chain, there is few tangle of a molecule at the time of melting, and orientation of it is carried out to an one direction only by receiving slight shearing stress, and even when it is liquefied, it shows the so-called liquid crystallinity which shows crystallinity.

Although it has the advantage which this liquid crystallinity polyester can apply the injection-molding processing method currently generally performed, and is excellent in fabrication nature, thermal resistance, dimensional stability, etc., for the orientation where the front face of the fabricated substrate is strong, the surface section

exfoliates, tends to produce fuzz, and if it remains as it is, it cannot perform secondary elaboration, such as vacuum deposition, ion plating, and sputtering.

Then, although it is possible to perform as pretreatment the surface roughening process by chemical which is used for the resin of the general former, chemically, a front face does not have the suitable solvent which is extremely affinitive with inactive, cannot remove a surface orientation layer, and cannot carry out surface roughening of the front face. Then, it is possible to add the inorganic filler and easily-elutable additive for weakening the strong stacking tendency of liquid crystalline polyester resin, and to roughen a front face with strong acid or a strong-base solution. However, even if it makes metallic coating form in all the front faces of the substrate etched by this approach by electroless deposition etc. If it is going to acquire the high adhesion force, for the irregularity on the front face of a substrate by which needed to raise surface roughness and metallic coating was carried out in this case extensively In the pattern sticking method by the dry film with which the profile section of the resist ink for circuit pattern formation fades, the unarrived section of ink is made, and a pattern is formed, it is inferior to the adhesion over the substrate of a film. Furthermore, metallic coating to the field where roughness is big is difficult for thickness not to become homogeneity but to form a precision thin line circuit in a subtractive process.

Moreover, when metallic coating was formed in the substrate which improved only the stacking tendency by direct vacuum deposition, sputtering, ion plating, etc., even if the smooth front face was obtained, the adhesion force of a coat could not present practical use with it highly. Especially, in common thermoplastics, the metallic film in which had much generating gas from the material in the inside of the vacuum at the time of performing vacuum deposition, sputtering, and ion plating, and it had the good engine performance was not able to be firmly stuck on resin. Although liquid crystallinity polyester has few problems of such generating gas, if it remains as it is, formation of a metal membrane which had the good adhesion force for said reason cannot be performed. Moreover, after adding the acid or the alkali soluble inorganic filler, for example and etching with an acid or alkali, even if it be going to form the precision thin line circuit with the subtractive process on the substrate which carried out electroless deposition and carried out whole surface metallic coating processing with the conventional method, Line width of face of 0.3mm and Space width of face of 0.30mm be limitations, if surface roughness be moreover improve for thinning, the adhesion force of a coat will become low, and practical use could not be presented with the conventional circuit.

In addition, the width of face of one circuit is indicated to be Line width of face, and spacing between **** bypasses is indicated to be Space width of face here.

On the other hand, liquid crystallinity polyester shows a low coefficient of linear expansion which is equal to the heat ray expansion coefficient of a common metal, has the description of not producing abnormalities, even if it is immersed in a 260-degree C pewter bath for 10 seconds in heatproof, and employs this property efficiently. Although the surface metal art which has improved said surface characteristic for the purpose of the application of the substrate which gave the components joined to the metal with adhesives and plating was called for, the still satisfying approach is not learned.

[The means for solving a technical problem]

this invention person etc. employs the useful description efficiently thermally [such liquid crystallinity polyester]. The surface which is easy to exfoliate, without spoiling physical and chemical property is not generated. The result wholeheartedly studied about the manufacture approach of the substrate whose precision thin line circuit formation gives the good metal membrane of adhesion to a substrate front face, and is attained with a subtractive process, The degree of hardness of the surface section in the condition of having lowered as much as possible while performing gas drainage of mold goods, heating the mold goods which consist of a constituent which made liquid crystallinity polyester containing an inorganic filler to specific temperature within a vacuum tub Sputtering, By carrying out surface metalizing by which approach of ion plating or vacuum deposition, it came to complete a header and this invention for the formation with firm adhesion of a metal membrane being possible, and formation of a thin line circuit very more precise than before being performed with a subtractive process.

Namely, this invention The manufacture approach of the substrate in which precision thin-line circuit formation is possible offers with the subtractive process characterized by for a front face to carry out metallic-coating processing by which approach of sputtering, ion plating, or vacuum deposition, heating the substrate which it comes to fabricate using the liquid-crystalline-polyester-resin constituent which makes the melting workability polyester (liquid-crystallinity polyester) which can form an anisotropy melting phase come to contain an inorganic filler so that the skin temperature of a substrate may become 60 degrees C or more within a vacuum tub. After the circuit forming method by the subtractive process here dissolves metals other than the conductor pattern section which covers the front face of the substrate which consists of conductive ingredients , such as a metal , with the acid-proof

ingredient which is etching resist for a part required as a conductor pattern extensively based on a circuit design to the substrate front face covering or after carrying out a laminating and by which etching resist is not cover with the etching reagent which fuses a metal , it is the approach of carrying out exfoliation removal of the etching resist with a chemical , making expose a conductor pattern , and forming a circuit .

One sort or two sorts or more of fines-like inorganic fillers chosen from the group which consists of an element of a periodic table II group element and its oxide, a sulfate, phosphate, silicate, a carbonate or aluminum, silicon, tin, lead, antimony, and a bismuth and its oxide are desirable, and the inorganic filler used by this invention has one sort chosen from the group which consists of the oxide, sulfate, the phosphate, and silicate of a periodic table II group element especially, or two desirable sorts or more

Sulfates are compounds, such as magnesium sulfate, a calcium sulfate, and a barium sulfate, the oxide of a periodic-table II group's element is **** compounds, such as magnesium oxide, a calcium oxide, barium oxide, and a zinc oxide, and especially phosphate is [phosphate is **** compounds such as magnesium phosphate, calcium phosphate, phosphoric-acid barium, phosphoric-acid zinc magnesium pyrophosphate, and pyrophosphoric-acid calcium, and / silicate is compounds, such as a magnesium silicate a calcium silicate, aluminum silicate, a kaolin talc, clay, diatomaceous earth, and wollastonite, and] suitable for it. Moreover, one sort chosen from the group which becomes the above etc. from the element of aluminum, silicon, tin, lead, antimony, and a bismuth and its oxide, or two sorts or more are desirable. Especially, metals, such as zinc, aluminum, tin, and lead, and the oxide of the metal are desirable.

The loadings of these fines-like inorganic fillers are 20 – 70 % of the weight preferably five to 80% of the weight to the liquid-crystalline-polyester-resin constituent whole quantity. At less than 5 % of the weight, a heterogeneous flow mark occurs on a mold-goods front face, and if a mold-goods surface sticks adhesive tape on a front face and it is torn off, peeling of the shape of a pellicle will produce it easily. It falls [on the other hand, if it exceeds 80 % of the weight, the fluidity of resin will fall, / mold goods with a good front face are not obtained, but / the mechanical strength of mold goods] to coincidence and is not desirable. moreover, inorganic fillers are fines-like -- desirable -- the particle size -- the range of 0.01-100-micrometer mean particle diameter -- 0.1-30-micrometer 0.5-10 micrometers are still more preferably suitable preferably. In less than 0.01 micrometers, it is easier to produce an aggregate on a mold-goods front face badly [distribution], if it exceeds 100 micrometers, the smooth

nature of mold goods will worsen, thinning for the precision circuit formation by the subtractive process becomes very difficult, and a still better appearance is not acquired.

Moreover, a fibrous inorganic substance is also desirable as an inorganic filler, and it is fibrous inorganic substance independent, or is used combining the above-mentioned fines-like inorganic filler.

As a fibrous inorganic substance, inorganic fiber-like matter, such as a fibrous object of metals, such as a glass fiber, a milled glass fiber, a carbon fiber, an asbestos fiber, a silica fiber, a silica alumina fiber, an alumina fiber, a zirconia fiber, a boron nitride fiber, **-ized silicon fiber, a boron fiber, a potassium titanate fiber and also stainless steel, aluminum, titanium, copper, and brass, is mentioned. Moreover, especially as the configuration, the thing in the range of 10 micrometers – 100 micrometers is desirable the diameter of 1–30 micrometers, and die length of 5 micrometers – 1mm.

Especially the fibrous inorganic substance used preferably is a glass fiber, and the loadings are 1 – 60% of the weight of the range to the total weight of a mold-goods constituent, and are 5 – 40 % of the weight preferably. When especially the glass fiber was combined with said fines-like inorganic filler, it was found out that it is contrary to anticipation, equalize the front face of mold goods further, and the adhesion force of plating for forming a conductive circuit on mold goods improves. Especially the milled glass fiber that hits in the middle of a glass fiber and fines-like glass from the field of the balance of the mechanical physical properties of surface roughness and an ingredient is desirable.

However, it is not desirable from fabrication nature and various kinds of physical-properties sides that the total loadings of said inorganic filler and concomitant use inorganic substance exceed 85 % of the weight in a mold-goods constituent.

The surface metallic-coating approach in this invention is the dry type metallization using a vacuum system, and, specifically, means the approach of giving a direct metal membrane to a resin shaping substrate by which approach of sputtering, ion plating, or vacuum deposition. Moreover, it makes to heat resin mold goods in temperature of 60 degrees C or more especially in this invention into an indispensable condition, and whenever [stoving temperature] is 150 degrees C or more desirably. However, in order to avoid that mold goods carry out softening deformation, it is desirable to limit to 270 degrees C or less.

Desirable temperature conditions change somewhat also with surface metallic-coating approaches, and are 200–250 degrees C in 60–200 degrees C and

vacuum deposition in 150–250 degrees C and ion plating in sputtering. although there be little generating of the gas within a vacuum tub compared with other ingredients as for the description , and the liquid crystallinity polyester use for this invention obtain the metal thin film which had good adhesion by approaches , such as sputtering , ion plating , or vacuum deposition , even when it remain as it is , it remove the gas which occur from resin mold goods , and can improve further adhesion on the resin front face of a metal atom by heat using the fall of the resin surface hardness by make it an elevated temperature . In addition, as for above-mentioned surface metalizing, it is desirable to make the inside of a tub into the bottom of the vacuum condition of 10⁻⁵ – 10⁻⁷Torr, and to perform it.

Although Line width of face of 0.30mm and Space width of face of 0.30mm of the conventional circuit were limitations as aforementioned, thinning with a Line width of face [of 0.25mm or less] and a Space width of face of 0.25mm or less of ***** becomes possible with the surface metal approach of this invention, and there is adhesion force of a circuit, and it came to be able to perform formation of the precision thin line circuit by the subtractive process.

The liquid crystallinity polyester of this invention is melting workability polyester, and it has the property to take an parallel array with a regular polymer chain in the state of melting. A molecule often calls the condition of having arranged in this way the nematic phase of a liquid crystal condition or the liquid crystallinity matter. Generally such a polymer molecule is long and slender, flat, and in accordance with the major axis of a molecule, its rigidity is quite high, and it consists of a polymer which has two or more chain expanding association which usually has the same axle or one of parallel relation.

The property of an anisotropy melting phase can be checked by the polarization detection method of common use using a rectangular polarizer. The check of an anisotropy melting phase uses a Leitz polarization microscope, and, more specifically, can be carried out by observing the melting sample put on the Leitz hot stage by one 40 times the scale factor of this under nitrogen-gas-atmosphere mind. When it inspects between rectangular polarizers, even if the polymer of this invention is a melting quiescent state, polarization will be penetrated and will show an anisotropy optically.

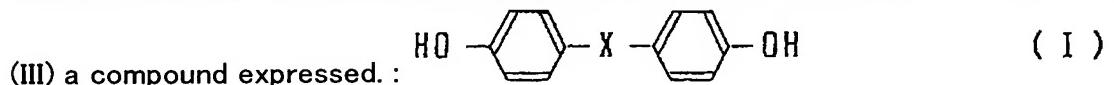
The liquid crystallinity polymer suitable for using it for this invention shows an insoluble inclination substantially to a common solvent, therefore is unsuitable for solution processing. However, as already stated, these polymers are easily processible by the ordinary melting processing method.

It is an example also with aromatic polyester and aromatic series polyester amide desirable [the polymer which shows the anisotropy melting phase used by this invention], and the desirable polyester that contains partially aromatic polyester and aromatic series polyester amide in the same chain.

It is the liquid crystallinity aromatic polyester and liquid crystallinity aromatic series polyester amide which have especially at least one or more sorts of compounds chosen from the group of an aromatic series hydroxyl carboxylic acid, an aromatic series hydroxylamine, and aromatic series diamine as a constituent preferably.

More specifically, it is 1. Polyester 2 which mainly consists of one sort of aromatic series hydroxycarboxylic acid and its derivative, or two sorts or more Mainly One sort or two sorts or more, and b aromatic series dicarboxylic acid of a aromatic series hydroxycarboxylic acid and its derivative, One sort or two sorts or more, and c aromatic series diol of alicycle group dicarboxylic acid and its derivative, Polyester 3 which consists of at least one sort of alicycle group diol, aliphatic series diol, and its derivative, or two sorts or more Mainly One sort or two sorts or more, and b aromatic series hydroxy amine of a aromatic series hydroxycarboxylic acid and its derivative, One sort or two sorts or more, and c aromatic series dicarboxylic acid of aromatic series diamine and its derivative, Polyester amide 4 which consists of one sort of alicycle group dicarboxylic acid and its derivative, or two sorts or more Mainly One sort or two sorts or more, and b aromatic series hydroxy amine of a aromatic series hydroxycarboxylic acid and its derivative, One sort or two sorts or more, and c aromatic series dicarboxylic acid of aromatic series diamine and its derivative, The polyester amide which consists of at least one sort of one sort or two sorts or more and d aromatic series diol of alicycle group dicarboxylic acid and its derivative, alicycle group diol, aliphatic series diol, and its derivative or two sorts or more is mentioned. Furthermore, a regulator may be used together if needed to the above-mentioned constituent.

The desirable example of the concrete compound which constitutes the liquid crystallinity polyester of this invention is biphenyl compounds, such as naphthalene compound [, such as 2, 6-naphthalene dicarboxylic acid, 2, 6-dihydroxy naphthalene, 1, and 4-dihydroxy naphthalene and a 6-hydroxy-2-naphthoic acid], 4, and 4-diphenyl dicarboxylic acid, 4, and 4-dihydroxy biphenyl, the following general formula (I), (II), or



(However, X: Radical chosen from alkylene (C1-C4), alkylidene, -O-, -SO-, -SO2-, -S-, radical Y:-(CH₂)_{n-} (n=1-4) chosen from -CO-, and -O(CH₂)_nO- (n=1-4))

It is the benzenoid of meta-position permutations, such as benzenoids of para-position permutations, such as para hydroxybenzoic acid, a terephthalic acid, hydroquinone, para aminophenol, and p-phenylene diamine, and those nuclear substitution benzenoids (a substituent is chosen from chlorine, a bromine, methyl, phenyl, and 1-phenylethyl), isophthalic acid, and resorcinol.

Moreover, the liquid crystallinity polyester used for this invention may be polyalkylene terephthalate which does not show an anisotropy melting phase partially in the same chain of everything but an above-mentioned constituent. The carbon numbers of the alkyl group in this case are 2 thru/or 4.

It is the still more desirable example which contains one sort or two sorts or more of compounds chosen from a naphthalene compound, a biphenyl compound, and para-position permutation benzenoid among above-mentioned constituents as an indispensable constituent. Moreover, it is an example with especially as desirable inside of permutation benzenoid, para hydroxybenzoic acid, methyl hydroquinone, and 1-phenylethyl hydroquinone as p-.

The example of the polyester which forms a desirable anisotropy melting phase in being used by the example and this invention of a compound which have the functional group of an ester plasticity used as a constituent is indicated by JP,63-36633,B.

suitable liquid crystallinity polyester to use by this invention -- general -- weight average molecular weight -- about 2,000-200,000 -- desirable -- about 10,000-50,000 -- it is about 20,000-25,000 especially preferably. aromatic series polyester amide suitable on the other hand -- general -- molecular weight -- about 5,000-50,000 -- it is about 10,000-30,000, 15,000-17,000, preferably. [for example,] Measurement of this molecular weight can be carried out by carrying out the quantum of the end group about gel permeation chromatography and a standard measuring method without solution formation of other polymers, for example, a compression-molding film, by infrared spectroscopy. Moreover, it can be made a pentafluoro phenol solution and molecular weight can also be measured using light scattering measurement.

the time of dissolving above-mentioned aromatic polyester and polyester amide in a pentafluoro phenol by concentration 0.1% of the weight by 60 degrees C again -- at least -- the logarithm of about 2.0 dl/g, for example, about 2.0 to 10.0 dl/g, -- generally viscosity (I. V.) is shown.

In this invention, it is the purpose which improves various properties and, in addition to the above-mentioned specific inorganic filler (a fines-like inorganic filler and fibrous inorganic substance), other concomitant use inorganic substances of various kinds of

can be blended further. In order to obtain the substrate excellent in properties, such as a mechanical property, thermal resistance, and dimensional stability (deformation-proof, camber), as for this concomitant use inorganic substance, blending is desirable, and according to the purpose, the shape of a powder and a tabular concomitant use inorganic substance are used for this.

As a powder-like inorganic substance, carbon black, a black smoke, a silica, quartz powder, a glass bead, glass balun, glass powder, the oxide of the metal like an iron oxide, other ferrites, silicon carbide, silicon nitride, boron nitride, etc. are mentioned. Moreover, as a tabular inorganic substance, a mica, a glass flake, various kinds of metallic foils, etc. are mentioned.

these concomitant use inorganic substances -- a kind -- or two or more sorts can be used together.

It is not desirable from fabrication nature and various kinds of physical-properties sides that the total loadings of said inorganic filler and concomitant use inorganic substance exceed 85 % of the weight in a mold-goods constituent. It is desirable to use a convergence agent or a finishing agent in use of the aforementioned inorganic filler and a concomitant use inorganic substance, if required.

Furthermore, the constituent of this invention may add other thermoplastics auxiliary to extent which does not spoil the purpose to mean in the range of this invention.

In this case, although especially the thermoplastics to be used is not limited, if an example is shown, polyolefines, such as polyethylene and polypropylene, polyacetal (a-gly or copolymer), polystyrene, a polyvinyl chloride, polyacrylic ester and those copolymers, a polyamide, a polycarbonate, ABS, polyphenylene oxide, a polyphenylene sulfide, a fluororesin, etc. can be mentioned. Moreover, two or more sorts can use these thermoplastics, mixing.

Furthermore, lubricant, lubricant, a crystallization accelerator (nucleating additive), etc. for an improvement of coloring agents, such as stabilizers, such as the well-known matter added by common thermoplastics and thermosetting resin, i.e., a plasticizer, an antioxidant, and an ultraviolet ray absorbent, an antistatic agent, a finishing agent, a surfactant, a flame retarder, a color, and a pigment, and a fluidity, and a mold-release characteristic can be suitably used according to the military requirement made into the purpose.

[The example of fruit **]

Although an example is given below and this invention is explained still more concretely, this invention is not limited to this.

Examples 1-14, examples 1-6 of a comparison After having carried out kneading

distribution of the filler (the value over the whole quantity for a constituent is shown% of the weight) shown in various below-mentioned liquid-crystalline-polyester-resin A-F and below-mentioned Table -1 by the melting kneading approach by the extruder, pelletizing and drying at 140 degrees C for 3 hours, the 50mmx70mmx3mm plate was fabricated using the metal mold by which temperature control was carried out to 100-160 degrees C with the making machine.

Substrate temperature was changed about the fabricated plate (substrate), and surface metalization processing was carried out by the following various approaches.

1) Vacuum deposition : the plate fabricated in the vacuum tub of a vacuum evaporation system (EX500 made from a Japanese vacuum technology) was set, and the inside of a vacuum tub was vacuated to 4×10^{-6} Torr.

Using the halogen lamp for mold-goods heating formed in the vacuum tub, the skin temperature of mold goods turned into predetermined temperature, the appearance set was carried out, metal copper was evaporated by the electron beam method, and the metal copper thin film (3-5 micrometers of thickness) was made to form on the surface of a substrate. The shaping plate was taken out after cooling the substrate after vacuum evaporationo.

Sputtering : 2) Use a sputtering system (made in the Tokuda factory 8ES) similarly. After high-vacuum-izing the inside of a vacuum tub to 3×10^{-6} Torr, setting up argon gas so that a sink and the equilibrium pressure force might be set to 5×10^{-3} Torr and setting substrate temperature as predetermined temperature with a halogen lamp It was made to rotate by rotational frequency 10rpm of a substrate, using the metal copper target, sputtering was performed to the mold goods set to the substrate so that it might become the location of 100mm from a target, and the metal copper thin film was made to form.

3) Ion plating : arc discharge mold ion plating system After making the inside of a vacuum tub into a high vacuum to 3×10^{-6} Torr using AIF-850SB (Shinko Seiki Co., Ltd.), and setting to predetermined temperature the mold goods on the substrate set in the tub, thin film formation of the metal copper was carried out by ion plating. Ionizing current was carried out by 100mA and the evaporation rate was carried out at 0.5-micrometer speed for /.

Since the shaping plate by which surface metalizing was carried out cannot measure peeling strength if it remains as it is, after having carried out electrolytic copper plating immediately after processing and making it form it in 30-40 micrometers of thickness, it was cut with the knife so that it might become band-like [of 5mm width of face], and measured peeling strength with the spring balance. It tore off and the

rate was made into 50 mm/min. A result is shown in Table -1.

In addition, liquid crystallinity polyester A-F used in the example has the following configuration unit.

[Effect of the Invention]

According to the surface metal approach of the liquid-crystalline-polyester-resin mold goods of this invention, to the appearance described above Do not cause surface exfoliation of the resin concerned easily, but it has a uniform and precise surface structure. In strength and old thermoplastics, without producing elevated-temperature exfoliation according the adhesion force of a surface metal membrane to the difference of a coefficient of thermal expansion with the difficult metal Circuit formation which it was precise and carried out thinning with the subtractive process (circuit width of face Line width of face of 0.25mm or less) Space width of face of 0.25mm or less became possible, pewter immersion (processing-time about 10 seconds) was also attained, and the expansion of exterior parts to the application for a printed-circuit board was attained from the first.

TECHNICAL PROBLEM

[Description of the Prior Art]

Unlike the thermoplastic polyester generally known, for example, polybutylene terephthalate, and polyethylene terephthalate, liquid crystallinity polyester consists of an upright macromolecule, and also in the state of melting, since the shape of a rod is maintained that it is hard to bend, as for a chain, there is few tangle of a molecule at the time of melting, and orientation of it is carried out to an one direction only by receiving slight shearing stress, and even when it is liquefied, it shows the so-called liquid crystallinity which shows crystallinity.

Although it has the advantage which this liquid crystallinity polyester can apply the injection-molding processing method currently generally performed, and is excellent in fabrication nature, thermal resistance, dimensional stability, etc., for the orientation where the front face of the fabricated substrate is strong, the surface section exfoliates, tends to produce fuzz, and if it remains as it is, it cannot perform secondary elaboration, such as vacuum deposition, ion plating, and sputtering.

Then, although it is possible to perform as pretreatment the surface surface roughening process by chemical which is used for the resin of the general former, chemically, a front face does not have the suitable solvent which is extremely affinitive with inactive, cannot remove a surface orientation layer, and cannot carry

out surface roughening of the front face. Then, it is possible to add the inorganic filler and easily-elutable additive for weakening the strong stacking tendency of liquid crystalline polyester resin, and to roughen a front face with strong acid or a strong-base solution. However, even if it makes metallic coating form in all the front faces of the substrate etched by this approach by electroless deposition etc. If it is going to acquire the high adhesion force, for the irregularity on the front face of a substrate by which needed to raise surface roughness and metallic coating was carried out in this case extensively In the pattern sticking method by the dry film with which the profile section of the resist ink for circuit pattern formation fades, the unarrived section of ink is made, and a pattern is formed, it is inferior to the adhesion over the substrate of a film. Furthermore, metallic coating to the field where roughness is big is difficult for thickness not to become homogeneity but to form a precision thin line circuit in a subtractive process.

Moreover, when metallic coating was formed in the substrate which improved only the stacking tendency by direct vacuum deposition, sputtering, ion plating, etc., even if the smooth front face was obtained, the adhesion force of a coat could not present practical use with it highly. Especially, in common thermoplastics, the metallic film in which had much generating gas from the material in the inside of the vacuum at the time of performing vacuum deposition, sputtering, and ion plating, and it had the good engine performance was not able to be firmly stuck on resin. Although liquid crystallinity polyester has few problems of such generating gas, if it remains as it is, formation of a metal membrane which had the good adhesion force for said reason cannot be performed. Moreover, after adding the acid or the alkali soluble inorganic filler, for example and etching with an acid or alkali, even if it be going to form the precision thin line circuit with the subtractive process on the substrate which carried out electroless deposition and carried out whole surface metallic coating processing with the conventional method, Line width of face of 0.3mm and Space width of face of 0.30mm be limitations, if surface roughness be moreover improve for thinning, the adhesion force of a coat will become low, and practical use could not be presented with the conventional circuit.

In addition, the width of face of one circuit is indicated to be Line width of face, and spacing between **** bypasses is indicated to be Space width of face here.

On the other hand, liquid crystallinity polyester shows a low coefficient of linear expansion which is equal to the heat ray expansion coefficient of a common metal, has the description of not producing abnormalities, even if it is immersed in a 260-degree C pewter bath for 10 seconds in heatproof, and employs this property efficiently.

Although the surface metal art which has improved said surface characteristic for the purpose of the application of the substrate which gave the components joined to the metal with adhesives and plating was called for, the still satisfying approach is not learned.

MEANS

[The means for solving a technical problem]

this invention person etc. employs the useful description efficiently thermally [such liquid crystallinity polyester]. The surface which is easy to exfoliate, without spoiling physical and chemical property is not generated. The result wholeheartedly studied about the manufacture approach of the substrate whose precision thin line circuit formation gives the good metal membrane of adhesion to a substrate front face, and is attained with a subtractive process, The degree of hardness of the surface section in the condition of having lowered as much as possible while performing gas drainage of mold goods, heating the mold goods which consist of a constituent which made liquid crystallinity polyester containing an inorganic filler to specific temperature within a vacuum tub Sputtering, By carrying out surface metalizing by which approach of ion plating or vacuum deposition, it came to complete a header and this invention for the formation with firm adhesion of a metal membrane being possible, and formation of a thin line circuit very more precise than before being performed with a subtractive process.

Namely, this invention The manufacture approach of the substrate in which precision thin-line circuit formation is possible offers with the subtractive process characterized by for a front face to carry out metallic-coating processing by which approach of sputtering, ion plating, or vacuum deposition, heating the substrate which it comes to fabricate using the liquid-crystalline-polyester-resin constituent which makes the melting workability polyester (liquid-crystallinity polyester) which can form an anisotropy melting phase come to contain an inorganic filler so that the skin temperature of a substrate may become 60 degrees C or more within a vacuum tub. After the circuit forming method by the subtractive process here dissolves metals other than the conductor pattern section which covers the front face of the substrate which consists of conductive ingredients , such as a metal , with the acid-proof ingredient which is etching resist for a part required as a conductor pattern extensively based on a circuit design to the substrate front face covering or after carrying out a laminating and by which etching resist is not cover with the etching

reagent which fuses a metal , it is the approach of carrying out exfoliation removal of the etching resist with a chemical , making expose a conductor pattern , and forming a circuit .

One sort or two sorts or more of fines-like inorganic fillers chosen from the group which consists of an element of a periodic table II group element and its oxide, a sulfate, phosphate, silicate, a carbonate or aluminum, silicon, tin, lead, antimony, and a bismuth and its oxide are desirable, and the inorganic filler used by this invention has one sort chosen from the group which consists of the oxide, sulfate, the phosphate, and silicate of a periodic table II group element especially, or two desirable sorts or more

Sulfates are compounds, such as magnesium sulfate, a calcium sulfate, and a barium sulfate, the oxide of a periodic-table II group's element is **** compounds, such as magnesium oxide, a calcium oxide, barium oxide, and a zinc oxide, and especially phosphate is [phosphate is **** compounds such as magnesium phosphate, calcium phosphate, phosphoric-acid barium, phosphoric-acid zinc magnesium pyrophosphate, and pyrophosphoric-acid calcium, and / silicate is compounds, such as a magnesium silicate a calcium silicate, aluminum silicate, a kaolin talc, clay, diatomaceous earth, and wollastonite, and] suitable for it. Moreover, one sort chosen from the group which becomes the above etc. from the element of aluminum, silicon, tin, lead, antimony, and a bismuth and its oxide, or two sorts or more are desirable. Especially, metals, such as zinc, aluminum, tin, and lead, and the oxide of the metal are desirable.

The loadings of these fines-like inorganic fillers are 20 – 70 % of the weight preferably five to 80% of the weight to the liquid-crystalline-polyester-resin constituent whole quantity. At less than 5 % of the weight, a heterogeneous flow mark occurs on a mold-goods front face, and if a mold-goods surface sticks adhesive tape on a front face and it is torn off, peeling of the shape of a pellicle will produce it easily. It falls [on the other hand, if it exceeds 80 % of the weight, the fluidity of resin will fall, / mold goods with a good front face are not obtained, but / the mechanical strength of mold goods] to coincidence and is not desirable. moreover, inorganic fillers are fines-like -- desirable -- the particle size -- the range of 0.01–100-micrometer mean particle diameter -- 0.1–30-micrometer 0.5–10 micrometers are still more preferably suitable preferably. In less than 0.01 micrometers, it is easier to produce an aggregate on a mold-goods front face badly [distribution], if it exceeds 100 micrometers, the smooth nature of mold goods will worsen, thinning for the precision circuit formation by the subtractive process becomes very difficult, and a still better appearance is not acquired.

Moreover, a fibrous inorganic substance is also desirable as an inorganic filler, and it is fibrous inorganic substance independent, or is used combining the above-mentioned fines-like inorganic filler.

As a fibrous inorganic substance, inorganic fiber-like matter, such as a fibrous object of metals, such as a glass fiber, a milled glass fiber, a carbon fiber, an asbestos fiber, a silica fiber, a silica alumina fiber, an alumina fiber, a zirconia fiber, a boron nitride fiber, **-ized silicon fiber, a boron fiber, a potassium titanate fiber and also stainless steel, aluminum, titanium, copper, and brass, is mentioned. Moreover, especially as the configuration, the thing in the range of 10 micrometers – 100 micrometers is desirable the diameter of 1–30 micrometers, and die length of 5 micrometers – 1mm.

Especially the fibrous inorganic substance used preferably is a glass fiber, and the loadings are 1 – 60% of the weight of the range to the total weight of a mold-goods constituent, and are 5 – 40 % of the weight preferably. When especially the glass fiber was combined with said fines-like inorganic filler, it was found out that it is contrary to anticipation, equalize the front face of mold goods further, and the adhesion force of plating for forming a conductive circuit on mold goods improves. Especially the milled glass fiber that hits in the middle of a glass fiber and fines-like glass from the field of the balance of the mechanical physical properties of surface roughness and an ingredient is desirable.

However, it is not desirable from fabrication nature and various kinds of physical-properties sides that the total loadings of said inorganic filler and concomitant use inorganic substance exceed 85 % of the weight in a mold-goods constituent.

The surface metallic-coating approach in this invention is the dry type metallization using a vacuum system, and, specifically, means the approach of giving a direct metal membrane to a resin shaping substrate by which approach of sputtering, ion plating, or vacuum deposition. Moreover, it makes to heat resin mold goods in temperature of 60 degrees C or more especially in this invention into an indispensable condition, and whenever [stoving temperature] is 150 degrees C or more desirably. However, in order to avoid that mold goods carry out softening deformation, it is desirable to limit to 270 degrees C or less.

Desirable temperature conditions change somewhat also with surface metallic-coating approaches, and are 200–250 degrees C in 60–200 degrees C and vacuum deposition in 150–250 degrees C and ion plating in sputtering.

although there be little generating of the gas within a vacuum tub compared with other ingredients as for the description , and the liquid crystallinity polyester use for this

invention obtain the metal thin film which had good adhesion by approaches , such as sputtering , ion plating , or vacuum deposition , even when it remain as it is , it remove the gas which occur from resin mold goods , and can improve further adhesion on the resin front face of a metal atom by heat using the fall of the resin surface hardness by make it an elevated temperature . In addition, as for above-mentioned surface metalizing, it is desirable to make the inside of a tub into the bottom of the vacuum condition of 10⁻⁵ – 10⁻⁷Torr, and to perform it.

Although Line width of face of 0.30mm and Space width of face of 0.30mm of the conventional circuit were limitations as aforementioned, thinning with a Line width of face [of 0.25mm or less] and a Space width of face of 0.25mm or less of ***** becomes possible with the surface metal approach of this invention, and there is adhesion force of a circuit, and it came to be able to perform formation of the precision thin line circuit by the subtractive process.

The liquid crystallinity polyester of this invention is melting workability polyester, and it has the property to take an parallel array with a regular polymer chain in the state of melting. A molecule often calls the condition of having arranged in this way the nematic phase of a liquid crystal condition or the liquid crystallinity matter. Generally such a polymer molecule is long and slender, flat, and in accordance with the major axis of a molecule, its rigidity is quite high, and it consists of a polymer which has two or more chain expanding association which usually has the same axle or one of parallel relation.

The property of an anisotropy melting phase can be checked by the polarization detection method of common use using a rectangular polarizer. The check of an anisotropy melting phase uses a Leitz polarization microscope, and, more specifically, can be carried out by observing the melting sample put on the Leitz hot stage by one 40 times the scale factor of this under nitrogen-gas-atmosphere mind. When it inspects between rectangular polarizers, even if the polymer of this invention is a melting quiescent state, polarization will be penetrated and will show an anisotropy optically.

The liquid crystallinity polymer suitable for using it for this invention shows an insoluble inclination substantially to a common solvent, therefore is unsuitable for solution processing. However, as already stated, these polymers are easily processible by the ordinary melting processing method.

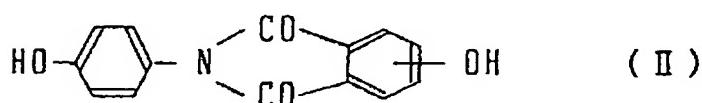
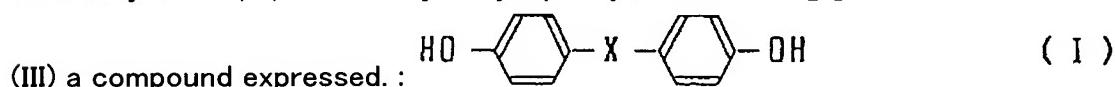
It is an example also with aromatic polyester and aromatic series polyester amide desirable [the polymer which shows the anisotropy melting phase used by this invention], and the desirable polyester that contains partially aromatic polyester and

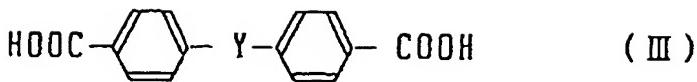
aromatic series polyester amide in the same chain.

It is the liquid crystallinity aromatic polyester and liquid crystallinity aromatic series polyester amide which have especially at least one or more sorts of compounds chosen from the group of an aromatic series hydroxyl carboxylic acid, an aromatic series hydroxylamine, and aromatic series diamine as a constituent preferably.

More specifically, it is 1. Polyester 2 which mainly consists of one sort of aromatic series hydroxycarboxylic acid and its derivative, or two sorts or more Mainly One sort or two sorts or more, and b aromatic series dicarboxylic acid of a aromatic series hydroxycarboxylic acid and its derivative, One sort or two sorts or more, and c aromatic series diol of alicycle group dicarboxylic acid and its derivative, Polyester 3 which consists of at least one sort of alicycle group diol, aliphatic series diol, and its derivative, or two sorts or more Mainly One sort or two sorts or more, and b aromatic series hydroxy amine of a aromatic series hydroxycarboxylic acid and its derivative, One sort or two sorts or more, and c aromatic series dicarboxylic acid of aromatic series diamine and its derivative, Polyester amide 4 which consists of one sort of alicycle group dicarboxylic acid and its derivative, or two sorts or more Mainly One sort or two sorts or more, and b aromatic series hydroxy amine of a aromatic series hydroxycarboxylic acid and its derivative, One sort or two sorts or more, and c aromatic series dicarboxylic acid of aromatic series diamine and its derivative, The polyester amide which consists of at least one sort of one sort or two sorts or more and d aromatic series diol of alicycle group dicarboxylic acid and its derivative, alicycle group diol, aliphatic series diol, and its derivative or two sorts or more is mentioned. Furthermore, a regulator may be used together if needed to the above-mentioned constituent.

The desirable example of the concrete compound which constitutes the liquid crystallinity polyester of this invention is biphenyl compounds, such as naphthalene compound [, such as 2, 6-naphthalene dicarboxylic acid, 2, 6-dihydroxy naphthalene, 1, and 4-dihydroxy naphthalene and a 6-hydroxy-2-naphthoic acid], 4, and 4-diphenyl dicarboxylic acid, 4, and 4-dihydroxy biphenyl, the following general formula (I), (II), or





(However, X: Radical chosen from alkylene (C1-C4), alkylidene, -O-, -SO-, -SO₂-, -S-, radical Y:-(CH₂)_n- (n=1-4) chosen from -CO-, and -O(CH₂)_nO- (n=1-4))

It is the benzenoid of meta-position permutations, such as benzenoids of para-position permutations, such as para hydroxybenzoic acid, a terephthalic acid, hydroquinone, para aminophenol, and p-phenylene diamine, and those nuclear substitution benzenoids (a substituent is chosen from chlorine, a bromine, methyl, phenyl, and 1-phenylethyl), isophthalic acid, and resorcinol.

Moreover, the liquid crystallinity polyester used for this invention may be polyalkylene terephthalate which does not show an anisotropy melting phase partially in the same chain of everything but an above-mentioned constituent. The carbon numbers of the alkyl group in this case are 2 thru/or 4.

It is the still more desirable example which contains one sort or two sorts or more of compounds chosen from a naphthalene compound, a biphenyl compound, and para-position permutation benzenoid among above-mentioned constituents as an indispensable constituent. Moreover, it is an example with especially as desirable inside of permutation benzenoid, para hydroxybenzoic acid, methyl hydroquinone, and 1-phenylethyl hydroquinone as p-.

The example of the polyester which forms a desirable anisotropy melting phase in being used by the example and this invention of a compound which have the functional group of an ester plasticity used as a constituent is indicated by JP,63-36633,B.

suitable liquid crystallinity polyester to use by this invention -- general -- weight average molecular weight -- about 2,000-200,000 -- desirable -- about 10,000-50,000 -- it is about 20,000-25,000 especially preferably. aromatic series polyester amide suitable on the other hand -- general -- molecular weight -- about 5,000-50,000 -- it is about 10,000-30,000, 15,000-17,000, preferably. [for example,] Measurement of this molecular weight can be carried out by carrying out the quantum of the end group about gel permeation chromatography and a standard measuring method without solution formation of other polymers, for example, a compression-molding film, by infrared spectroscopy. Moreover, it can be made a pentafluoro phenol solution and molecular weight can also be measured using light scattering measurement.

the time of dissolving above-mentioned aromatic polyester and polyester amide in a pentafluoro phenol by concentration 0.1% of the weight by 60 degrees C again -- at

least -- the logarithm of about 2.0 dl/g, for example, about 2.0 to 10.0 dl/g, -- generally viscosity (I. V.) is shown.

In this invention, it is the purpose which improves various properties and, in addition to the above-mentioned specific inorganic filler (a fines-like inorganic filler and fibrous inorganic substance), other concomitant use inorganic substances of various kinds of can be blended further. In order to obtain the substrate excellent in properties, such as a mechanical property, thermal resistance, and dimensional stability (deformation-proof, camber), as for this concomitant use inorganic substance, blending is desirable, and according to the purpose, the shape of a powder and a tabular concomitant use inorganic substance are used for this.

As a powder-like inorganic substance, carbon black, a black smoke, a silica, quartz powder, a glass bead, glass balun, glass powder, the oxide of the metal like an iron oxide, other ferrites, silicon carbide, silicon nitride, boron nitride, etc. are mentioned. Moreover, as a tabular inorganic substance, a mica, a glass flake, various kinds of metallic foils, etc. are mentioned.

these concomitant use inorganic substances -- a kind -- or two or more sorts can be used together.

It is not desirable from fabrication nature and various kinds of physical-properties sides that the total loadings of said inorganic filler and concomitant use inorganic substance exceed 85 % of the weight in a mold-goods constituent. It is desirable to use a convergence agent or a finishing agent in use of the aforementioned inorganic filler and a concomitant use inorganic substance, if required.

Furthermore, the constituent of this invention may add other thermoplastics auxiliary to extent which does not spoil the purpose to mean in the range of this invention.

In this case, although especially the thermoplastics to be used is not limited, if an example is shown, polyolefines, such as polyethylene and polypropylene, polyacetal (a gay or copolymer), polystyrene, a polyvinyl chloride, polyacrylic ester and those copolymers, a polyamide, a polycarbonate, ABS, polyphenylene oxide, a polyphenylene sulfide, a fluororesin, etc. can be mentioned. Moreover, two or more sorts can use these thermoplastics, mixing.

Furthermore, lubricant, lubricant, a crystallization accelerator (nucleating additive), etc. for an improvement of coloring agents, such as stabilizers, such as the well-known matter added by common thermoplastics and thermosetting resin, i.e., a plasticizer, an antioxidant, and an ultraviolet ray absorbent, an antistatic agent, a finishing agent, a surfactant, a flame retarder, a color, and a pigment, and a fluidity, and a mold-release characteristic can be suitably used according to the military

requirement made into the purpose.

[The example of fruit **]

Although an example is given below and this invention is explained still more concretely, this invention is not limited to this.

Examples 1-14, examples 1-6 of a comparison After having carried out kneading distribution of the filler (the value over the whole quantity for a constituent is shown% of the weight) shown in various below-mentioned liquid-crystalline-polyester-resin A-F and below-mentioned Table -1 by the melting kneading approach by the extruder, pelletizing and drying at 140 degrees C for 3 hours, the 50mmx70mmx3mm plate was fabricated using the metal mold by which temperature control was carried out to 100-160 degrees C with the making machine.

Substrate temperature was changed about the fabricated plate (substrate), and surface metalization processing was carried out by the following various approaches.

1) Vacuum deposition : the plate fabricated in the vacuum tub of a vacuum evaporation system (EX500 made from a Japanese vacuum technology) was set, and the inside of a vacuum tub was vacuated to 4×10^{-6} Torr.

Using the halogen lamp for mold-goods heating formed in the vacuum tub, the skin temperature of mold goods turned into predetermined temperature, the appearance set was carried out, metal copper was evaporated by the electron beam method, and the metal copper thin film (3-5 micrometers of thickness) was made to form on the surface of a substrate. The shaping plate was taken out after cooling the substrate after vacuum evaporationo.

Sputtering : 2) Use a sputtering system (made in the Tokuda factory 8ES) similarly. After high-vacuum-izing the inside of a vacuum tub to 3×10^{-6} Torr, setting up argon gas so that a sink and the equilibrium pressure force might be set to 5×10^{-3} Torr and setting substrate temperature as predetermined temperature with a halogen lamp It was made to rotate by rotational frequency 10rpm of a substrate, using the metal copper target, sputtering was performed to the mold goods set to the substrate so that it might become the location of 100mm from a target, and the metal copper thin film was made to form.

3) Ion plating : arc discharge mold ion plating system After making the inside of a vacuum tub into a high vacuum to 3×10^{-6} Torr using AIF-850SB (Shinko Seiki Co., Ltd.), and setting to predetermined temperature the mold goods on the substrate set in the tub, thin film formation of the metal copper was carried out by ion plating. Ionizing current was carried out by 100mA and the evaporation rate was carried out at 0.5-micrometer speed for /.

Since the shaping plate by which surface metalizing was carried out cannot measure peeling strength if it remains as it is, after having carried out electrolytic copper plating immediately after processing and making it form it in 30–40 micrometers of thickness, it was cut with the knife so that it might become band-like [of 5mm width of face], and measured peeling strength with the spring balance. It tore off and the rate was made into 50 mm/min. A result is shown in Table -1.

In addition, liquid crystallinity polyester A–F used in the example has the following configuration unit.

(19)日本国特許庁 (JP)

(12) 特 許 公 報 (B 2)

(11)特許番号

第2714440号

(45)発行日 平成10年(1998)2月16日

(24)登録日 平成9年(1997)10月31日

(51)Int.Cl.⁶
H 0 5 K 1/03

識別記号
6 1 0

府内整理番号
F I
H 0 5 K 1/03

技術表示箇所
6 1 0 M

(21)出願番号 特願平1-143464

(22)出願日 平成1年(1989)6月6日

(65)公開番号 特開平3-8388

(43)公開日 平成3年(1991)1月16日

(73)特許権者 99999999
ボリプラスチックス株式会社
大阪府大阪市中央区安土町2丁目3番13
号
(72)発明者 鈴木 好治
静岡県庵原郡富士川町中野台1-3-2
(72)発明者 明田 智行
静岡県富士市宮島885-11
(74)代理人 弁理士 古谷 馨

審査官 川端 修

(54)【発明の名称】精密細線回路用基板の製造方法

1

(57)【特許請求の範囲】

【請求項1】異方性溶融相を形成しうる溶融加工性ポリエスチル(液晶性ポリエスチル)に無機充填材を含有せしめてなる液晶性ポリエスチル樹脂組成物を用いて成形してなる基板を、真空槽内で基板の表面温度が60°C以上となるよう加熱しながらスパッタリング、イオンプレーティング又は真空蒸着の何れかの方法により表面金属被覆処理することを特徴とするサブトラクティブ法により精密細線回路形成可能な基板の製造方法。

【請求項2】無機充填材が周期律表II族元素及びその酸化物、硫酸塩、リン酸塩、珪酸塩、炭酸塩、又はアルミニウム、珪素、スズ、鉛、アンチモン、ビスマスの元素及びその酸化物からなる群より選ばれた1種又は2種以上の微粉状無機充填材であり、その配合量が組成物全重量に対して5~80重量%である請求項1記載の基板の製

2

造方法。

【請求項3】微粉状無機充填材が平均粒径0.01~100μmの範囲にある請求項2記載の基板の製造方法。

【請求項4】無機充填材が直径1~30μm、長さ5μm~1mmの範囲にある纖維状無機物であり、その配合量が組成物全重量に対して1~60重量%である請求項1記載の基板の製造方法。

【請求項5】無機充填材が周期律表II族元素及びその酸化物、硫酸塩、リン酸塩、珪酸塩、炭酸塩、又はアルミニウム、珪素、スズ、鉛、アンチモン、ビスマスの元素及びその酸化物からなる群より選ばれた1種又は2種以上の微粉状無機充填材と纖維状無機物とを併用したものであり、これらの総配合量が組成物全重量に対して85重量%以下である請求項1記載の基板の製造方法。

【請求項6】纖維状無機物がガラス纖維、ミルドガラス

ファイバー又はチタン酸カリウム繊維である請求項4又は5記載の基板の製造方法。

【請求項7】基板が射出成形、押出成形及び圧縮成形のうちから選ばれる成形加工手段により成形されたものである請求項1記載の基板の製造方法。

【請求項8】基板がピングリッドアレイ(PGA)用又は成形プリント配線用基板である請求項1記載の基板の製造方法。

【請求項9】基板が立体形状、フィルム状又はシート状である請求項1記載の基板の製造方法。

【請求項10】請求項1～9の何れかの製造方法により得られたサブトラクティブ法により精密細線回路形成可能な基板。

【発明の詳細な説明】

〔産業上の利用分野〕

本発明は、異方性溶融相を形成し得る溶融加工性ポリエスチル「以後単に「液晶性ポリエスチル」と略す」樹脂組成物を用いて成形してなるサブトラクティブ法による精密細線回路が形成可能な基板の表面金属被覆処理法とその処理法により得られる基板に関する。

更に詳しくは、サブトラクティブ法による精密細線回路形成用基板として耐熱性、成形加工性に優れた液晶性ポリエスチル樹脂組成物を用いて成形した基板に、効率よく表面金属被覆処理する方法とその方法により作成された基板に関する。

〔従来の技術とその課題〕

液晶性ポリエスチルは、一般に知られている熱可塑性ポリエスチル、例えばポリブチレンテレフタレート、ポリエチレンテレフタレートと異なり、剛直な高分子よりも、溶融状態でも分子鎖は折れ曲がり難く棒状を保っているため、溶融時に分子の絡み合いが少なく、僅かな剪断応力を受けるだけで一方向に配向し、液状でも結晶性を示すいわゆる液晶性を示す。

斯かる液晶性ポリエスチルは一般に行われている射出成形加工法を適用することができ、成形加工性、耐熱性、寸法安定性等に優れる利点を有するが、成形された基板の表面は強い配向のため表層部は剥離し毛羽立ちを生じ易く、そのままでは真空蒸着、イオンプレーティング、スペッタリング等の2次加工ができない。

そこで、従来一般の樹脂に用いられている様な薬品による表面粗面化処理を前処理として行うことが考えられるが、表面は化学的には極めて不活性で親和性のある適切な溶剤がなく、表層の配向層を取り除き表面を粗面化することができない。そこで液晶性ポリエスチル樹脂の強い配向性を弱めるための無機フィラーや易溶出性添加剤を加えて、強酸や強アルカリ溶液により表面を粗化することが考えられる。然しながら、この方法でエッチングした基板の全表面に金属被覆を無電解メッキ等により形成せしめても、高い密着力を得ようとすれば、表面粗度を上げていく必要があり、この場合は全面的に金属被

覆された基板表面の凹凸のために、回路パターン形成のためのレジストインキの輪郭部がボケたり、インキの未着部ができ、又パターンの形成されるドライフィルムによるパターン貼付け法においてはフィルムの基板に対する密着性に劣る。更に粗度の大きな面への金属被覆は膜厚が均一にならず、サブトラクティブ法では精密細線回路を形成することは困難である。

また、配向性だけを改良した基板に直接真空蒸着、スペッタリング、イオンプレーティング等により金属被覆を形成した場合は、平滑な表面は得られても皮膜の密着力は高くなく、実用に供し得なかった。特に、一般の熱可塑性樹脂では真空蒸着、スペッタリング、イオンプレーティングを行う際の真空中での素材からの発生ガスが多く、良好な性能を持った金属皮膜を樹脂の上に強固に密着させることができなかつた。液晶性ポリエスチルはこのような発生ガスの問題は少ないと、そのままでは前記理由により良好な密着力を持った金属膜の形成ができない。また、例えば酸又はアルカリ易溶性無機フィラーを添加して酸又はアルカリでエッチングした後、常法で無電解メッキして全面金属被覆処理した基板上にサブトラクティブ法で精密細線回路を形成しようとしても、従来の回路はLine幅0.3mm、Space幅0.30mmが限界であり、しかも細線化のため表面粗度を改善していくと被膜の密着力が低くなり、実用に供し得なかつたのである。

尚、ここでLine幅とは回路一本の幅、Space幅とは隣合う回路間の間隔を示す。

一方、液晶性ポリエスチルは、一般金属の熱線膨張係数に匹敵する低い線膨張係数を示し、耐熱的には260℃のハンダ浴に10秒間浸漬しても異常を生じない等の特徴を有し、この特性を生かして、接着剤により金属と接合した部品やメッキを付与した基板の用途を目的として前記表面特性を改善した表面金属処理方法が求められていたが、未だ満足のいく方法は知られていない。

〔課題を解決するための手段〕

本発明者等は、この様な液晶性ポリエスチルの熱的に有益な特徴を生かし、物理的・化学的性質を損なうことなしに剥離し易い表層を発生させず、基板表面に密着性の良好な金属膜を付与してサブトラクティブ法で精密細線回路形成が可能となる基板の製造方法について鋭意研究した結果、液晶性ポリエスチルに無機充填材を含有せしめた組成物からなる成形品を真空槽内で特定温度に加熱しながら成形品のガス抜きを行うと同時に表層部の硬度をできるだけ下げた状態でスペッタリング、イオンプレーティング又は真空蒸着の何れかの方法により表面金属処理することにより、強固な密着性を持つ金属膜の形成が可能であり、サブトラクティブ法により従来よりも極めて精密な細線回路の形成が出来ることを見出し、本発明を完成するに至った。

即ち本発明は

異方性溶融相を形成しうる溶融加工性ポリエスチル

5

(液晶性ポリエステル)に無機充填材を含有せしめてなる液晶性ポリエステル樹脂組成物を用いて成形してなる基板を、真空槽内で基板の表面温度が60°C以上となるよう加熱しながらスパッタリング、イオンプレーティング又は真空蒸着の何れかの方法により表面の金属被覆処理することを特徴とするサブトラクティブ法により精密細線回路形成可能な基板の製造方法を提供するものである。

ここでいうサブトラクティブ法による回路形成法とは、金属等の導電性材料よりなる基板の表面を全面的に被覆又は積層した後、基板表面に回路設計に基づく導体パターンとして必要な部分をエッチングレジストである耐酸性材料で被覆し、金属を溶融するエッチング液でエッチングレジストが被覆されていない導体パターン部以外の金属を溶解した後、エッチングレジストを薬品で剥離除去して導体パターンを露出させ回路を形成する方法である。

本発明で用いられる無機充填材とは、周期律表II族元素及びその酸化物、硫酸塩、リン酸塩、珪酸塩、炭酸塩、又はアルミニウム、珪素、スズ、鉛、アンチモン、ビスマスの元素及びその酸化物からなる群より選ばれた1種又は2種以上の微粉状無機充填材が好ましく、特に周期律表II族元素の酸化物、硫酸塩、リン酸塩及び珪酸塩からなる群より選ばれる1種又は2種以上が好ましい。

周期律表II族の元素の酸化物とは、酸化マグネシウム、酸化カルシウム、酸化バリウム、酸化亜鉛等の如き化合物であり、リン酸塩とはリン酸マグネシウム、リン酸カルシウム、リン酸バリウム、リン酸亜鉛、ピロリン酸マグネシウム、ピロリン酸カルシウム等の如き化合物であり、硫酸塩とは硫酸マグネシウム、硫酸カルシウム、硫酸バリウム等の化合物であり、珪酸塩とは珪酸マグネシウム、珪酸カルシウム、珪酸アルミニウム、カオリン、タルク、クレー、珪藻土、ウォラストナイト等の化合物であり、特にリン酸塩が好適である。又、上記他にアルミニウム、珪素、スズ、鉛、アンチモン、ビスマスの元素及びその酸化物からなる群より選ばれた1種又は2種以上も好ましい。特に、亜鉛、アルミニウム、スズ、鉛等の金属及びその金属の酸化物が好ましい。

これらの微粉状無機充填材の配合量は液晶性ポリエステル樹脂組成物全量に対して5~80重量%、好ましくは20~70重量%である。5重量%未満では成形品表面に不均質な流れマークが発生し、成形品表層は粘着テープを表面に貼り付け引き剥がすと容易に薄皮状の剥がれが生じる。一方、80重量%を超えると樹脂の流動性が低下し、表面の良好な成形品が得られず、同時に成形品の機械的強度も低下してしまい好ましくない。又、無機充填材は微粉状であるのが好ましく、その粒径は平均粒径0.01~100μmの範囲、好ましくは0.1~30μm、更に好ましくは0.5~10μmが適切である。0.01μm未満では分

6

散不良により成形品表面に凝集塊が生じ易く、100μmを超えると成形品の平滑性が悪くなり、サブトラクティブ法による精密回路形成のための細線化が極めて困難となり、更に良い外観が得られない。

又、無機充填材として繊維状無機物も好ましく、繊維状無機物単独で、若しくは上記微粉状無機充填材と組み合わせて使用される。

繊維状無機物としては、ガラス繊維、ミルドガラスファイバー、炭素繊維、アスベスト繊維、シリカ繊維、シリカ・アルミナ繊維、アルミナ繊維、ジルコニア繊維、窒化硼素繊維、塑化珪素繊維、硼素繊維、チタン酸カリウム繊維、更にステンレス、アルミニウム、チタン、銅、真鍮等の金属の繊維状物などの無機繊維状物質が挙げられる。又、その形状としては、直径1~30μm、長さ5μm~1mm、特に10μm~100μmの範囲にあるものが好ましい。

特に好ましく用いられる繊維状無機物はガラス繊維であり、その配合量は成形品組成物の全重量に対し、1~60重量%の範囲であり、好ましくは5~40重量%である。特にガラス繊維を前記微粉状無機充填材に組み合わせると、予想に反し成形品の表面は一層均一化して、成形品上に導電性回路を形成するためのメッキの密着力が向上することが見出された。表面粗度と材料の機械的物性のバランスの面からガラス繊維と微粉状ガラスの中間に当たるミルドガラスファイバーが特に好ましい。

ただし、前記無機充填材と併用無機物との総配合量が成形品組成物中の85重量%を越えることは成形加工性及び各種の物性面から好ましくない。

本発明における表面金属被覆処理法とは、真空系を用いた乾式金属被覆法のこと、具体的には、スパッタリング、イオンプレーティング又は真空蒸着の何れかの方法により樹脂成形基板に直接金属膜を付与する方法をいう。また、本発明では特に樹脂成形品を60°C以上の温度に加熱することを必須条件とし、加熱温度は望ましくは150°C以上である。但し、成形品が軟化変形することを避けるため270°C以下にとどめるのが好ましい。

好ましい温度条件は表面金属被覆処理法によつても多少異なり、スパッタリングにおいては150~250°C、イオンプレーティングにおいては60~200°C、真空蒸着においては200~250°Cである。

本発明に使用する液晶性ポリエステルは、他の材料に比べて真空槽内でのガスの発生が少ないのが特徴であり、そのままでもスパッタリング、イオンプレーティング又は真空蒸着等の方法により良好な密着性をもつた金属薄膜を得るが、加熱することにより、樹脂成形品から発生するガスを取り除き、高温にすることによる樹脂表面硬度の低下を利用して、金属原子の樹脂表面への付着を一層改良できる。尚、上記表面金属処理は、槽内を10⁻⁷~10⁻⁶Torrの真空条件下にして行うのが望ましい。

前記の通り、従来の回路はLine幅0.30mm、Space幅0.3

50

0mmが限界であったが、本発明の表面金属処理法により回路幅はLine幅0.25mm以下、Space幅0.25mm以下の細線化が可能となり、かつ回路の密着力もあり、サブトラクティブ法による精密細線回路の形成ができるようになった。

本発明の液晶性ポリエステルとは、溶融加工性ポリエステルで、溶融状態でポリマー分子鎖が規則的な平行配列をとる性質を有している。分子がこのように配列した状態をしばしば液晶状態または液晶性物質のネマチック相という。このようなポリマー分子は、一般に細長く、偏平で、分子の長軸に沿ってかなり剛性が高く、普通は同軸または平行のいずれかの関係にある複数の連鎖伸長結合を有しているようなポリマーからなる。

異方性溶融相の性質は、直交偏光子を利用した慣用の偏光検査法により確認することができる。より具体的には、異方性溶融相の確認は、Leitz偏光顕微鏡を使用し、Leitzホットステージにのせた溶融試料を窒素雰囲気下で40倍の倍率で観察することにより実施できる。本発明のポリマーは直交偏光子の間で検査したときにたとえ溶融静止状態であっても偏光は透過し、光学的に異方性を示す。

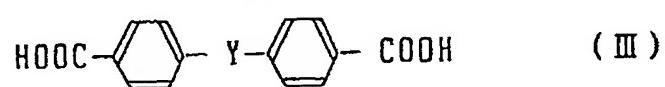
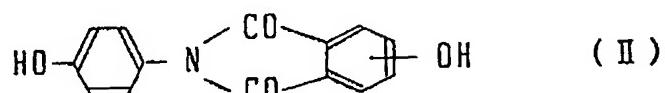
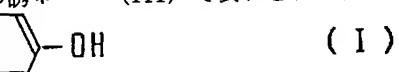
本発明に使用するのに適した液晶性ポリマーは、一般溶剤には実質的に不溶である傾向を示し、したがって溶液加工には向きである。しかし、既に述べたように、これらのポリマーは普通の溶融加工法により容易に加工することができる。

本発明で用いられる異方性溶融相を示すポリマーは、芳香族ポリエステル及び芳香族ポリエスチルアミドが好ましく、芳香族ポリエスチル及び芳香族ポリエスチルアミドを同一分子鎖中に部分的に含むポリエスチルも好ましい例である。

特に好ましくは、芳香族ヒドロキシカルボン酸、芳香族ヒドロキシルアミン、芳香族ジアミンの群から選ばれた少なくとも1種以上の化合物を構成成分として有する液晶性芳香族ポリエスチル、液晶性芳香族ポリエスチルアミドである。

より具体的には、

1) 主として芳香族ヒドロキシカルボン酸及びその誘*



(但し、X:アルキレン ($C_1 \sim C_4$)、アルキリデン、 $-O-$ 、 $-SO-$ 、 $-SO_2-$ 、 $-S-$ 、 $-CO-$ より選ばれる基
Y: $- (CH_2)_n -$ ($n = 1 \sim 4$)、 $-O-(CH_2)_n -$

$-O-$ ($n = 1 \sim 4$) より選ばれる基)
p-ヒドロキシ安息香酸、テレフタル酸、ハイドロキノン、p-アミノフェノール及びp-フェニレンジアミ

ン等のパラ位置換のベンゼン化合物及びそれらの核置換ベンゼン化合物（置換基は塩素、臭素、メチル、フェニル、1-フェニルエチルより選ばれる）、イソフタル酸、レゾルシン等のメタ位置換のベンゼン化合物である。

又、本発明に使用される液晶性ポリエステルは、上述の構成成分の他の同一分子鎖中に部分的に異方性溶融相を示さないポリアルキレンテレフタレートであってもよい。この場合のアルキル基の炭素数は2乃至4である。

上述の構成成分の内、ナフタレン化合物、ビフェニル化合物、パラ位置換ベンゼン化合物より選ばれる1種若しくは2種以上の化合物を必須の構成成分として含むものが更に好ましい例である。又、p-位置換ベンゼン化合物の内、p-ヒドロキシ安息香酸、メチルハイドロキノン及び1-フェニルエチルハイドロキノンは特に好ましい例である。

構成成分となるエステル形成性の官能基を有する化合物の具体例及び本発明で用いられるのに好ましい異方性溶融相を形成するポリエステルの具体例については特公昭63-36633号公報に記載されている。

本発明で用いるのに好適な液晶性ポリエステルは一般に重量平均分子量が約2,000～200,000、好ましくは約10,000～50,000、特に好ましくは約20,000～25,000である。一方、好適な芳香族ポリエステルアミドは一般に分子量が約5,000～50,000、好ましくは約10,000～30,000、例えば15,000～17,000である。かかる分子量の測定は、ゲルパーミエーションクロマトグラフィーならびに他のポリマーの溶液形成を伴わない標準的測定法、たとえば圧縮成形フィルムについて赤外分光法により末端基を定量することにより実施できる。また、ペンタフルオロフェノール溶液にして光散乱法を用いて分子量を測定することもできる。

上記の芳香族ポリエステル及びポリエステルアミドはまた、60°Cでペンタフルオロフェノールに0.1重量%濃度で溶解したときに、少なくとも約2.0dl/g、たとえば約2.0～10.0dl/gの対数粘度(I.V.)を一般に示す。

本発明においては、種々の特性を改良する目的で、上記特定の無機充填材（微粉状無機充填材及び繊維状無機物）に加え、更に他の各種の併用無機物を配合することができる。かかる併用無機物は機械的特性、耐熱性、寸法安定性（耐変形、そり）等の性質に優れた基板を得るためにには配合することが好ましく、これには目的に応じて粉粒状、板状の併用無機物が用いられる。

粉粒状無機物としては、カーボンブラック、黒煙、シリカ、石英粉末、ガラスピーズ、ガラスバルーン、ガラス粉、酸化鉄の如き金属の酸化物、その他フェライト、炭化珪素、窒化珪素、窒化硼素等が挙げられる。

又、板状無機物としては、マイカ、ガラスフレーク、各種の金属箔等が挙げられる。

これらの併用無機物は一種又は二種以上併用すること

ができる。

前記無機充填材と併用無機物との総配合量が成形品組成物中の85重量%を越えることは成形加工性及び各種の物理面から好ましくない。前記の無機充填材及び併用無機物の使用にあたっては必要ならば収束剤又は表面処理剤を使用することが望ましい。

更に本発明の組成物は、本発明の範囲でその意図する目的を損なわない程度に他の熱可塑性樹脂を補助的に添加したものであってもよい。

この場合に使用する熱可塑性樹脂は特に限定されないが、例を示すと、ポリエチレン、ポリプロピレン等のポリオレフィン、ポリアセタール（ホモ又はコポリマー）、ポリスチレン、ポリ塩化ビニル、ポリアクリル酸エステル、及びそれらの共重合体、ポリアミド、ポリカーボネート、ABS、ポリフェニレンオキシド、ポリフェニレンスルフィド、フッ素樹脂等を挙げることができる。またこれらの熱可塑性樹脂は2種以上混合して使用することができる。

更に一般的な熱可塑性樹脂及び熱硬化性樹脂に添加される公知の物質、即ち、可塑剤、酸化防止剤や紫外線吸収剤等の安定剤、帯電防止剤、表面処理剤、界面活性剤、難燃剤、染料や顔料等の着色剤及び流動性や離型性の改善のための滑剤、潤滑剤及び結晶化促進剤（核剤）等もその目的とする要求性能に応じ適宜使用することができる。

[実施例]

以下実施例をあげて本発明を更に具体的に説明するが、本発明はこれに限定されるものではない。

実施例1～14、比較例1～6

後述の各種液晶性ポリエステル樹脂A～Fと表-1に示した充填材（重量%は対組成物全量に対する値を示す）とを押出機による溶融混練方法により混練分散させペレット化し、140°Cで3時間乾燥した後、成形機により100～160°Cに温調された金型を用いて50mm×70mm×3mmの平板を成形した。

成形した平板（基板）について基板温度を変え、下記各種方法により表面金属化処理を実施した。

- 1) 真空蒸着：真空蒸着装置（日本真空技術製EX500）の真空槽内に成形した平板をセットし、真空槽内を 4×10^{-6} Torrまで真空化した。

真空槽内に設けた成形品加熱用ハロゲンランプを用い、成形品の表面温度が所定の温度になる様セットし、電子ビーム法により金属銅を蒸発させ、基板の表面に金属銅薄膜（膜厚3～5 μm）を形成させた。蒸着後基板を冷却した上で成形平板を取り出した。

- 2) スパッタリング：同様にスパッタリング装置（徳田製作所製8ES）を用い、真空槽内を 3×10^{-6} Torrまで高真空化した後、アルゴンガスを流し、平衡圧力が 5×10^{-3} Torrになる様に設定した上、基板温度をハロゲンランプにより所定の温度に設定した上で、基板の回転数10

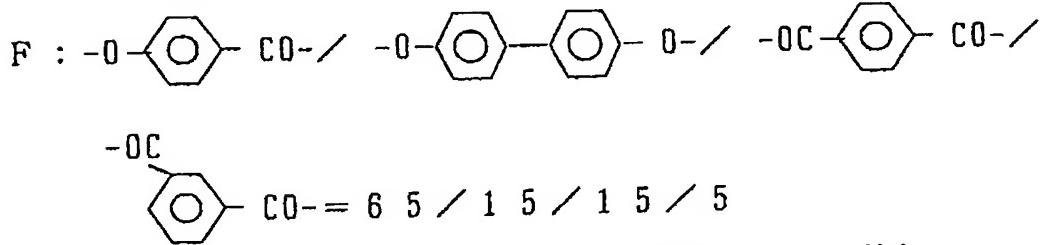
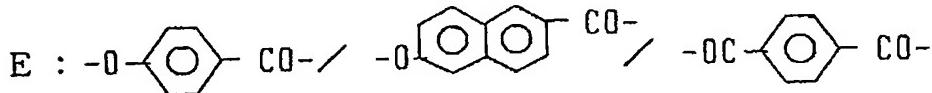
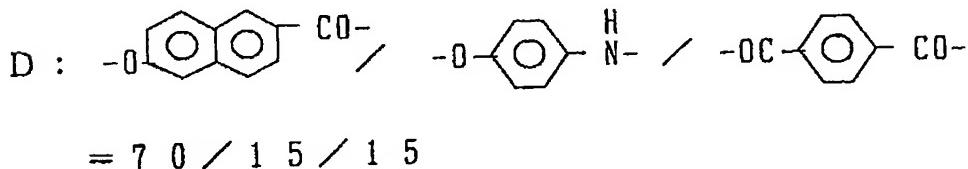
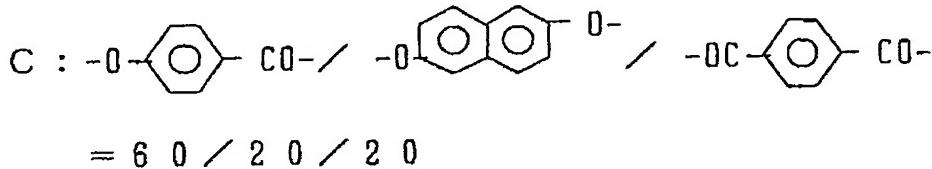
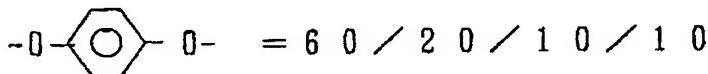
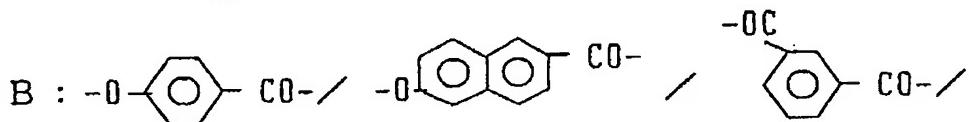
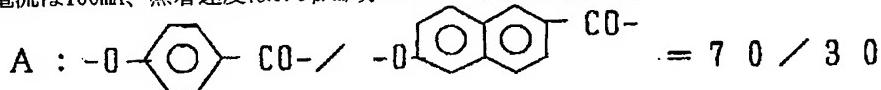
rpmで回転させ、金属銅ターゲットを用い、ターゲットから100mmの位置になる様に基板にセットした成形品にスパッタリングを行い、金属銅薄膜を形成させた。

3) イオンプレーティング：アーク放電型イオンプレーティング装置 AIF-850SB (神港精機株式会社) を用いて、真空槽内を 3×10^{-6} Torrまで高真空中にした後、槽内にセットされた基板上の成形品を所定の温度にセットした上へイオンプレーティングにより金属銅を薄膜形成させた。イオン化電流は100mA、蒸着速度は $0.5 \mu\text{m}/\text{分}$ の*

* スピードで実施した。

表面金属処理された成形平板はそのままではピーリング強さを測定できないため、処理後直ちに電気銅メッキを実施し、膜厚 $30\sim40 \mu\text{m}$ に形成させた後、5mm幅の帯状になる様にナイフでカットし、ピーリング強さをバネばかりにより測定した。引き剥がし速度は $50\text{mm}/\text{min}$ とした。結果を表-1に示す。

尚、実施例で使用した液晶性ポリエステルA～Fは下記構成単位を有するものである。



(以上の数字はモル比)

表 - 1

| 実施例 及び 比較例 | 材 料 | 表面金属処理方法・基板温度(℃) | | | | 金属被膜密着強さ (ピーリング強さ) kg/cm |
|------------------|------------------------------------|------------------|-----------|------------|--------|--------------------------------|
| | | 真空蒸着 | スパッタリング | イオンプレーティング | フライラーゲ | |
| 実施例 1 | ポリマー | フライラー (1) | フライラー (2) | — | — | — |
| 比較例 1 | A (50) ミルドファイバー (50) | — | — | 30 | — | 0.10 |
| 比較例 2 | A (50) " (15) ピコリン酸カルシウム (35) | — | — | — | — | 0.15 |
| 比較例 3 | A (50) " (50) ピコリン酸カルシウム (35) | — | — | 50 | — | 0.20 |
| 比較例 4 | A (50) " (15) ピコリン酸カルシウム (35) | — | — | 50 | — | 0.25 |
| 実施例 1 | A (50) " (50) ピコリン酸カルシウム (35) | — | — | 200 | — | 1.00 |
| 実施例 2 | A (50) " (15) ピコリン酸カルシウム (35) | — | — | 200 | — | 1.10 |
| 実施例 3 | A (50) " (15) " (35) | — | — | 250 | — | 1.20 |
| 実施例 4 | A (40) ガラスファイバー (30) ウォラストナイト (30) | — | — | 200 | — | 1.05 |
| 実施例 5 | A (70) チタン酸カリウム (30) ワイスカー (30) | — | — | 200 | — | — |
| 実施例 6 | A (40) 塩酸カルシウム (30) 酸化亜鉛 (30) | — | — | 200 | — | — |
| 実施例 7 | A (80) マイカ (20) | — | — | 200 | — | — |
| 比較例 5 | A (50) ミルドファイバー (50) | — | — | — | 40 | — |
| 実施例 8 | A (50) " (50) | — | — | — | 200 | — |
| 比較例 6 | A (50) " (50) | — | — | — | — | — |
| 実施例 9 | A (50) " (50) | — | — | — | — | — |
| 実施例 10 | B (50) " (50) | — | — | — | — | — |
| 実施例 11 | C (50) " (50) | — | — | — | 200 | — |
| 実施例 12 | D (50) " (50) | — | — | — | — | — |
| 実施例 13 | E (50) " (50) | — | — | — | 200 | — |
| 実施例 14 | F (50) " (50) | — | — | — | 200 | — |

[発明の効果]

以上述べた様に、本発明の液晶性ポリエステル樹脂成形品の表面金属処理法によれば、当該樹脂の表層剥離を容易に起こさず、均一で緻密な表面構造を持ち、表面金

属膜の密着力を強め、これまでの熱可塑性樹脂では困難であった金属との熱膨張係数の差による高温剥離を生じることもなく、サブトラクティブ法によって精密で細線化した回路形成（回路幅をLine幅0.25mm以下、Space幅

(8)

特許 2714440

15

0.25mm以下) が可能となり、ハンダ浸漬(処理時間約10秒)も可能となり、外装部品はもとより、プリント配線

16

基板を対象とした用途への展開が可能となった。